FORMATION AND MIGRATION OF ORGANIC IRON COMPOUNDS IN SOIL[1]

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The problems of the migration of iron have always attracted the attention of soil scientists because of the widespread distribution of the displacement and deposition of iron in nature and their great importance in the genesis of a number of soil groups (podzolic and swampy soils, soloths, solonetz, etc.), as well as the great complexity of these processes.

The majority of investigators recognize that water-soluble organic substances in the soil play an important role in the migration of iron (1, 2, 3, 7, 8, 13, 14, 15, 18, 20, 21, 22). Since the transformation of iron compounds in the soil is associated with the ability of iron to pass from the ferric to the ferrous form and back again, much attention has also been devoted to discovering the conditions governing the formation of ferrous iron compounds in the soil and the possibility of their movement (3, 4, 5, 6, 9, 10, 11). Most of the papers on this subject note the instability of the ferrous iron compounds in the soil because of their rapid transformation into the ferric form; this is the reason for the small role played by these forms in the migration of iron.

For a number of years the Department of Soil Science and the V. R. Vil'yams Museum of the K. A. Timiryazev Moscow Agricultural Academy, under the direction of S. P. Yarkov, have investigated the conditions of formation of soluble iron compounds and the possibility of the migration of iron in the soil (12, 20, 21, 22, 23).

This article presents results of a three-year observation of the dynamics of oxidation-reduction in sod-podzolic soils, as well as data on laboratory experiments to determine the possibility of the formation of organic iron compounds during the course of temporary reducing processes in the soil.[2]

It is known that ferrous iron compounds are formed as a result of biochemical processes during the course of temporary anaerobiosis in the soil. Laboratory experiments were conducted to study the ability of water-soluble organic products of the decomposition of plant residues to extract ferrous iron from gley soil. The method used in these experiments was as follows. Plant residues (fir needles, birch leaves, clover hay and timothy) in the amount of 25 g of air-dried material were decomposed under various conditions of moisture: optimal (aerobic conditions) and excess (anaerobic conditions). The magnitude of the oxidation-reduction potential served as the control for the anaerobic conditions. The durations of the experiments were 1 month, 3 months and 1 year.

At the conclusion of the experiments, water extracts with a ratio of 1:40 between the water and the original organic mass and with five-minute agitation were prepared from the plant residues in various stages of decomposition. The extracts were filtered and the pH, the sesquioxides and the organic matter recalculated as carbon were determined.

The extracts thus obtained were allowed to react with gley soil (sod-podzolic soil from the A_{plowed} horizon, 0-20 cm, in the fields of the Timiryazev Agricultural Academy farm) with a soil-solution ratio of 1:2.5. The organic matter and the FeO and Fe_2O_3 in the filtrate, the latter tw
α-α'-dipyridyl, were
of the experiments are given in Table 1. These figures show that in the decomposition of the plant residues under conditions of excess moisture a considerably greater quantity of water-soluble organic compounds is

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[2] Senior Laboratory Technicians M. N. Rytikova and A. F. Shemyakina took part in the analysis of the data.

formed, especially during the first period of decomposition (one month and three months). One may also note a definite regularity in the ability of the water-soluble products of the decomposition of plant residues to extract ferrous iron from gley soil. The products of anaerobic decomposition extract ferrous iron in much greater quantities. This important difference between the products of aerobic and anaerobic decomposition is observed in the reaction of gley soil both with original extracts from decomposed plant residues and with extracts containing equal amounts of organic matter in terms of carbon content. When plant residues, along with the determination of the iron content directly in the extract, the iron was determined in the same extract after the organic matter destruction by hydrogen peroxide. The results are given in Table 2.

Table 2 shows that in the reaction of the soil with the decomposition products of plant residues a large amount of iron combined with organic matter. The iron content is especially high in the case of the anaerobic decomposition products of fir needles.

The fixed iron is in the form of organic iron

Table 1

FeO extraction from gley soil by water-soluble products of plant residue decomposition

Plant residues	Conditions and stage of decomposition	pH	Organic matter in g C/l	FeO in mg/100 g absolutely dry soil — Solution — Original concentration	FeO in mg/100 g absolutely dry soil — Solution — Concentration adjusted for C
	One month				
Clover and timothy	Aerobic	7.9	0.142	3.4	1.8
	Anaerobic	5.15	0.414	8.15	6.8
Fir needles	Aerobic	5.55	0.065	5.4	5.4
	Anaerobic	5.32	0.241	6.0	3.26
Birch leaves	Aerobic	7.55	0.170	3.4	2.45
	Anaerobic	6.76	0.409	4.72	3.26
	Three months				
Clover and timothy	Aerobic	7.95	0.203	2.21	1.33
	Anaerobic	5.25	0.605	15.5	4.65
Fir needles	Aerobic	4.6	0.154	2.76	2.76
	Anaerobic	5.3	0.476	6.65	2.33
Birch leaves	Aerobic	5.65	0.248	3.32	1.66
	Anaerobic	6.4	0.767	2.21	2.33
	One year				
Clover and timothy	Aerobic	8.5	0.238	3.9	0.166
	Anaerobic	5.5	0.095	1.07	0.125
Fir needles	Aerobic	4.8	0.084	1.07	0.125
	Anaerobic	4.7	0.073	1.43	1.43
Birch leaves	Aerobic	7.2	0.223	1.07	0.18
	Anaerobic	6.7	0.270	1.43	0.125

gley soil reacted with water-soluble products of the decomposition of plant residues, different forms of iron, possessing different stabilities and thus different migrating capacities through the soil profile, pass into the extract. The most interesting in this regard are the so-called fixed forms of iron (18).

In order to determine the possibility of the formation of fixed forms of iron in the soil reaction with the decomposition products of compounds which are apparently mainly of a complex character. An electrodialysis was made by the authors (Table 3) to find the characteristic features of this condition.

The artificial solutions were obtained by the reaction of water-soluble products of the decomposition of plant residues on gley soil.

The natural solutions represent top water layers taken in peaty gley soil and carefully

Table 2

Content of fixed iron extracted by solutions from gley soil

Plant material	Decomposition conditions	FeO in mg/100 g soil		
		Filtrate		Fixed iron
		Before oxidation	After oxidation	
Clover and timothy	Aerobic	4.13	7.5	3.77
	Anaerobic	8.84	10.1	1.26
Fir needles	Aerobic	5.4	5.6	0.2
	Anaerobic	6.0	10.5	4.5
Birch leaves	Aerobic	4.8	9.0	4.2
	Anaerobic	7.66	7.75	2.09
Water extract	—	2.03	2.25	0.22

Table 3

Iron content in the anolyte in the dialysis of the solutions

Solutions	Dialysis duration, hours	Iron as FeO, mg/l	
		In original solution	In anolyte
	Artificial		
Experiment 1	10	107.0	48.5
Experiment 2	7	18.0	8.0
Experiment 3	7	14.0	traces
	Natural		
a) Top water layer taken in September	13	5.5	1.0
b) Top water layer taken in May	6	9.0	1.5

filtered through fine filters.

Electrodialysis of the top water layer and the artificial solutions has shown that the soluble iron combined with organic matter is not only a cation, but also enters into the composition of the complex organic-iron anion, as indicated by the presence of iron in the anolyte.

A.A. Rode (16) points out that this form of iron compound is evidently the simplest and the least dependent on the pH of the medium and on the concentration of Ca. The complex nature of such organic iron compounds is also confirmed by the results of experiments in the passage of these solutions through ion-exchange resins (KB-4, KU-2, AV-16) and by analysis of newly formed (legumes) sod-podzolic soils and soloths.

The forms of fixed iron are of primary importance in the migration of iron through the soil profile.

In one experiment, for example, the authors filtered a solution containing 30 mg of FeO/l, including 11 mg/l of fixed FeO, through a sod horizon sample forming a 10-cm layer. After the filtration, 14 mg/l of total FeO and 8 mg/l of fixed FeO were found in the solution.

Thus the unstable forms of ionic iron cannot migrate through the soil, whereas the fixed iron passes through the soil in considerable quantities.

Under the conditions of excess moisture, various ferrous iron compounds are formed in the soil, including soluble organic iron complex forms. Such water-soluble ferrous iron compounds under the conditions of

Table 4

Comparison of the properties of natural solutions and synthetic ferric iron

No.	Properties investigated	Natural solution	Synthetic salt
		Iron, %[a]	
1	Tyndall effect	Present	Present
2	Particle charge by the cataphoresis method	-	+
3	Qualitative reaction for Fe+++ without acidification	None	None
4	Solubility in 0.001 N HCl	None	None
	" " 0.005 "	66.7	None
	" " 0.01 "	100	Trace
	" " 0.05 "	100	6.5
5	Filtered by suction through Berkefel'd candles	85	None
	" through Pukal candles	41.3	None
	" through parchment filter	12.74	None
6	Adsorbed in passing through:		
	10 cm layer, with suction	100	100
	activated carbon	58.33	100
	illuvial horizon	41.66	100
	sod horizon	33.33	100
	podzolic horizon	25.00	100
	amorphous SiO_2	0.00	100
7	Precipitation of iron with a ratio of Fe_2O_3 to water-soluble humus from peat of:		
	1:3.14	None	100
	1:1.46	None	52
8	Precipitation of $Fe(OH)_3$ from natural solution obtained from soil with forest litter, with a 1:6.6 ratio of Fe_2O_3 to water-soluble humus	None during the course of one year	

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[a] For the investigation, solutions were used with the following concentrations of Fe_2O_3 in mg/l: No. 4 - 15.84, No. 5 - 28.94, No. 6 - 33.52, Nos. 7-8 - 15.80.

available oxygen may become ferric. To obtain such compounds for further study of their properties, the following procedure was used: 500 g of soil from the sod horizon, taken from areas with temporary excess moisture and containing a large amount of ferrous iron, were placed in a container and treated for ten minutes with distilled water with continuous agitation in a stream of carbon dioxide. The suspension was then filtered through large folded filters. The filtrate was allowed to stand until no negative reaction for Fe++ (with α-α'-dipyridyl) was observed. The solutions thus obtained had the external appearance of the weak iron salt usually prepared in the laboratory. The properties of the natural and artificial solutions of ferric iron were compared. The artificial iron salt was prepared as described by Aarnio (1). The iron was determined by the titanometric method.

The data in Table 4 show that both solutions have colloidal properties, confirmed by the presence of the Tyndall effect. In regard to the other properties associated with iron the solutions are essentially different. The artificial solution is a simple physicochemical system consisting of colloids of identical composition, whereas the natural solution is a complex system containing not only iron compounds but also a number of other water-soluble substances.

The lower oxide compounds removed from the soil by means of carbonic acid extraction may be both water-soluble minerals and organic forms of bi-valent iron. Oxidized mineral forms, which are represented mainly by ferrous bicarbonates, produce mineral colloids of iron hydroxide, and oxidized organic forms produce organic-mineral compounds of the type of the complex organic iron compounds. The entire system has a negative charge. The transition from the lower to the higher oxide is accompanied by the formation of compounds with various degrees of dispersion, as manifested by their ability to pass through filters with pores of different diameters.

The largest quantity of iron compounds in

Table 5

Dynamics of the oxidation-reduction potential (rH_2) and ferrous iron
(FeO in mg 100 g dry soil, extract of 0.1 N H_2SO_4 averaged over three years, 1955-1957)

Place sample taken	Horizon and depth, cm	April		May		June		July-Aug.		Sept.		Oct.		Nov.	
		rH_2	FeO	rH_2	FeO	rH_2	FeO	rH_2	FeO	rH_2	FeO	rH_2	FeO	rH_2	FeO
Section 1															
Dense birch forest. Soil strongly podzolized, fine clay loam on clay loam mantle.	A_0 0—4	20,5	21,4	29,0	27,0	28,8	3,6	29,3	2,12	27,0	5,7	27,1	4,6	27,8	6,0
	A_1 15—25	21,7	2,3	30,9	9,0	31,2	1,93	31,0	1,15	28,9	2,5	29,1	2,4	28,9	1,8
	B_1 45—55	24,2	0,27	32,2	3,2	32,1	1,4	32,7	0,5	29,9	1,5	32,1	0,13	31,6	2,1
Section 2															
Moss forest. Soil gley podzol on clay loam.	A_0 0—4	25,1	21,0	29,0	36,5	30,5	12,1	30,8	—	28,5	8,4	28,8	9,5	30,1	5,5
	A_1 4—8	24,4	8,0	28,8	31,7	31,7	7,0	32,3	7,0	30,3	3,4	29,9	2,06	29,3	2,0
	A_2 15—25	29,2	0,55	31,9	32,5	32,5	1,1	32,5	0,7	32,2	0,35	29,9	0,35	29,5	0,7
	B_1 45–55	Waterlogged		32,0	30,1	33,1	0,41	32,7	0,5	33,2	0,13	32,7	0,27	31,4	1,5
Section 3															
Dry meadow. Soil is sod-strongly podzolized gley fine clay loam on clay loam.	A_1 2—10	22,0	9,0	30,2	4,0	30,0	1,8	30,2	0,95	30,8	2,8	29,6	7,9	28,5	11,7
	A_2 15—25	26,0	14,0	31,0	0,4	32,1	1,5	31,7	0,40	32,0	2,3	30,2	13,8	30,7	1.6
	B_1 45—55	Waterlogged		32,6	0,54	33,8	0,42	33,7	0,45	32,7	0,3	31,9	11,0	32,2	3,35
Section 3-a															
Plowland. Soil sod-medium podzolized fine clay loam on clay loam.	A_p 0—3	24,2	5,8	31,5	0,9	32,1	0,5	31,0	0,55	30,1	0,56	30,5	0,45	30,5	0,46
	A_p 10—20	22,6	4,6	31,8	0,7	31,8	0,3	31,4	0,48	31,1	1,3	31,3	0,75	30,5	1,00
	A_2 25—35	23,2	5,0	31,5	1,25	31,5	0,25	31,0	0,38	30,5	0,32	31,3	1.7	30.6	0,43
	B_1 50—60	25,4	0.33	33,3	0,4	32,3	0,20	32,7	0,30	32,0	0,33	31,3	0,7	31.2	1,09

Note: Comma represents decimal point; A_p represents A_{plowed}.

the natural solution passes through the Berkefel'd filter candles (85%), about half the quantity through the Pukal' ultrafilter candles (41.5%), and a still smaller part of the iron compounds (12.7%) through the parchment filter in dialysis. This indicates the presence in the solution of finely dispersed or molecular solutions of organic iron complexes. The colloids in the artificial solution are entirely withheld by all the filters.

The ability of the iron in the natural solutions to pass easily into ionic form under weak acidification indicates that the oxidation of the ferrous forms of iron causes the formation of easily soluble forms of ferric iron such as the freshly deposited, strongly hydrated oxides and organic iron complexes. Table 4 shows that 0.005 N HCl reverts 66.7% of the iron in these compounds into ionic form, and with a 0.01 N HCl in the solution all the iron passes into the ionic form; only a very small amount (6.5%) of the iron in the artificial solution, however, is reverted into the ionic form with a 0.05 N HCl in the solution.

One of the important properties of the natural solutions is their very great stability. In the case of the ratios of iron to water-soluble humus examined (1:3.14 and 1:1.46) in the natural solutions there was no precipitation of iron, whereas in the synthetic salt, in the case of the first ratio the precipitation was complete and in the case of the second ratio quite large (52%). In working with the natural solutions a case was noted in which no iron was precipitated from the solution during a whole year.

The combination of all the properties of the natural solution (negative charge, high dispersion, high stability, etc.) is manifested in the ability of the iron compounds to pass through the soil in the form of similar solutions; this is shown by the data on the filtration of solutions through the various horizons of sod-podzolic soil (Table 5). On the basis of this information, one may acknowledge the possibility of the formation of mobile organic iron compounds wherever the conditions of anaerobiosis and biochemical reducing processes appear. The latter may be defined by the magnitude of the oxidation-reduction potential.

In studying the dynamic aspects of the oxidation-reduction processes under natural conditions, four permanent areas were chosen in the Krasnopolyana district (village of Belyy Rast) Moscow Oblast', where for three years systematic determinations were made throughout the soil profile of the oxidation-reduction potential, the mobile forms of ferrous and ferric iron, the mobile aluminum and the water-soluble organic matter. The results of the observations of the dynamics of rH_2 and ferrous iron are given in Table 5.

Table 5 shows that the oxidation-reduction conditions in soils under various types of growth show ~~of~~ seasonal nature. The lowest values of rH_2, indicating reducing conditions in the soil, are observed in the spring. The values of the oxidation-reduction potential reach their greatest magnitude in the summer, the absolute quantities indicating a predominance of oxidizing processes in the soil. In the autumn the magnitude of rH_2 again decreases somewhat. The clearest seasonal change in the oxidation-reduction potential appears in soil under forest. It must be noted that in all cases the magnitude of rH_2 increases downward through the soil profile, indicating an intensification of the oxidizing conditions in the lower horizons of the soil.

A similar regularity may be seen in the changes in the ferrous iron. The greatest amount is formed in spring under forest vegetation in the upper horizon of the soil -- i. e., during the period in which the lowest values of rH_2 are noted. With such interrelationships of rH_2 in the soil profile, the ferrous iron formed in the upper horizons, decreasing in amount as one moves to the lower horizons, may be oxidized and turned into the stable water-soluble organic iron complexes whose properties have been mentioned previously.

Thus the data from field and laboratory investigations show the possibility of the formation of mobile forms of iron during reducing processes under the conditions of temporary excess soil moisture. In their broadest aspect these processes take place in the soils of the taiga zone, where the iron (along with the H ion) is a hydromorphic element of the landscape (13). In the southern part of the forest-meadow zone the processes of iron migration are most clearly manifested only in the swampy moss forests.

In the steppe zone, the conditions for the migration of iron in the form of organic iron compounds are produced only in places where there is temporary excess moisture -- in steppe depressions, estuaries, and below fissures, where the formation of solonetz, soloths, solodized soils and the so-called depression podzolized soils are observed (22, 23).

CONCLUSIONS

1. In soils with temporary excess moisture, reducing processes appear during the spring that lead to the formation of ferrous iron.

2. The ferrous iron, reacting with water-soluble organic substances, forms complex

organic iron compounds. Upon later oxidation of the iron these compounds maintain a high stability and the ability of migrating through the soil.

3. There is a possibility of the formation of complex organic iron compounds under the conditions of the formation of podzolic and bog soils, as well as soloths, solonetz and depression podzolized soils.

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